

Cross-Reference To Related Application

Field of the Invention

Background of the Invention

The present non-dripping, flame retardant insulative compositions are fluoroelastomers with nanocomposite and flame retardant additives. The

present compositions can be melt processed to form extruded articles. Such manufacturing process and the resulting articles also constitute a portion of the inventive contribution disclosed herein.

It is known that the incorporation of nanocomposite additives into fluoroelastomeric compositions can improve some of properties of the compositions, particularly combustion properties including non-dripping characteristics. The nanocomposites that are suitable for incorporation into the present compositions are preferably montmorillonites (the main fraction of the clay mineral bentonite), which are layered aluminosilicate or magnesium-silicate materials whose individual platelets measure on the order of one micron diameter, giving them an aspect ratio of about 1000:1. It is this morphology that leads to increased barrier properties to moisture, resistance of the composition to deformation, resistance to whitening or blooming, improved mechanical strength, sizeable drop in heat release rate and smoke properties, improved flame retardancy and char integrity of the polymer compositions. The nanocomposite additives are preferably chemically modified to increase the hydrophobicity of their surfaces, thereby enhancing their fire performance effectiveness. It is also known that blending or alloying fluoroelastomeric compositions with suitable olefinic or polyvinylchloride (PVC) polymers improves the flexibility, electrical properties,

and manufacturing costs of the resulting blend or alloy. Suitable polymers to make the blends and alloys of the present compositions are:

polytetrafluoroethylene (PTFE) fluorocarbons,
fluorinated ethylene/propylene (FEP)
fluorocarbons, perfluoroalkoxy (PFA)
fluorocarbons, ethylene tetrafluoroethylene (ETFE)
fluoropolymers, polyvinylidene (PVDF)
fluoropolymers, ethylene chlorotrifluoroethylene
(ECTFE) fluoropolymers, fluoro-chlorinated
homopolymers, copolymers and terpolymers, very low
density polyethylene (VLDPE), low density
polyethylene (LDPE), linear low density
polyethylene (LLDPE), high density polyethylene
(HDPE), polypropylene (PP), ethylene propylene
copolymer or rubber (EPR), ethyl vinyl acetate
(EVA), ethylene ethyl acrylate (EEA), ethylene
methyl acrylate (EMA), ethylene butyl acrylate
(EBA), and ethylene-based homopolymers, copolymers
and terpolymers, and PVC-based homopolymers,
copolymers and terpolymers.

The use of various flame retardant additives such as molybdates, metal hydrates, oxides, carbonates, talcs, clays, borates, stannates, phosphates, silicates, graphites, and carbon blacks will provide the resulting products with enhanced combustion properties.

The present fluoroelastomeric compositions may be crosslinked or grafted by any convenient method, such as by chemical crosslinking using organic peroxides, irradiation, and organosilanes

or chemical grafting using acrylic and maleic acid.

The present thermoplastic fluoroelastomeric compositions have a high limiting oxygen index (LOI), and also burn with no visible smoke and/or dripping. The combination of favorable combustion, electrical and physical properties make the present compositions suitable for many applications such as cable components employed in market segments such as telecommunication, signal, power, industrial, and military cables.

Summary of the Invention

The present non-dripping, flame retardant, fluoroelastomeric compositions comprise:

- (a) a fluoropolymeric base polymer; and
- (b) a nanoclay additive.

The preferred fluoropolymeric base polymer is selected from the group consisting of polytetrafluoroethylene (PTFE) fluorocarbons, fluorinated ethylene/propylene (FEP) fluorocarbons, perfluoroalkoxy (PFA) fluorocarbons, ethylene tetrafluoroethylene (ETFE) fluoropolymers, polyvinylidene (PVDF) fluoropolymers, ethylene chlorotrifluoroethylene (ECTFE) fluoropolymers, and fluoro-chlorinated homopolymers, copolymers and terpolymers.

The preferred composition further comprises at least one of an olefinic polymer, one of an acetate resin and an acrylate resin, and a polyvinylchloride resin.

The preferred olefinic polymer is selected from the group consisting of very low density polyethylene (VLDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), polypropylene (PP), and ethylene propylene rubber (EPR). The group from which said olefinic polymer is selected can further consist of ethylene-based homopolymers, copolymers and terpolymers. The at least one olefinic polymer can be crosslinked, preferably using an organic peroxide.

The preferred one of an acetate resin and an acrylate resin is selected from the group consisting of ethyl vinyl acetate (EVA), ethylene ethyl acrylate (EEA), ethylene methyl acrylate (EMA), and ethylene butyl acrylate (EBA).

The preferred nanoclay additive is selected from the group consisting of synthetic silicate montmorillonites, natural layered silicate montmorillonites and a layered alumina-silicate. The individual platelets of the preferred nanoclay additive are approximately 1 micron in diameter. The nanoclay additive is preferably chemically modified to increase its hydrophobicity.

The preferred composition further comprises a filler selected from the group consisting of metal hydrates, oxides, carbonates, talcs, clays, molybdates, borates, stannates, carbon blacks, silicates, and phosphates.

The preferred composition may also further comprise an additive comprising at least one

substance selected from the group consisting of an antioxidant, a pigment, and a lubricant.

A method for preparing an exfoliated thermoplastic elastomer blend of a fluoropolymer and a nanocomposite comprising dynamically mixing the fluoropolymer and the nanocomposite in a ratio of from about 99:1 to about 50:50 parts by weight, respectively. In the preferred method, at least one of an antioxidant, a lubricant and a pigment contacts said blend during mixing.

Detailed Description Of The Preferred Embodiments

Two primary parameters that effectively define the performance levels of data communication cables are electrical and combustion properties. Balancing these parameters is important to achieving optimal performance. Over the last few years, it has become apparent that the telecommunication industry is entering a period of revolutionary change. The challenge facing the telecommunication cable manufacturers is to comply with the higher data transmission speeds. The present compositions can be employed to provide solutions to the foregoing concerns from a material and cable design viewpoint.

Common telecommunication cable types include: (NEC Article 725) CL2: communication class 2 cables, CL2R: communication class 2 riser cables, CL2P: communication class 2 plenum cables, CL3: communication class 3 cables, CL3R: communication class 3 riser cables, CL3P: communication class3

The first part of the book is devoted to a general discussion of the theory of the firm, and the second part to a more detailed analysis of the role of the firm in the economy. The book is written in a clear and concise style, and is suitable for both students and researchers.

The blends of the present composition comprise an important additive, namely, nanocomposites. The principal components of polymeric nanocomposites are water-swellaable synthetic and natural layered silicates such as montmorillonites (the main fraction of the clay mineral bentonite). These polymeric nanocomposites are commonly employed and are commercially available in different types. The high aspect ratio (edge length:thickness of layer) of the layers strongly influences the properties of the polymeric composition. To obtain the value of the properties, the layers have to be separated (exfoliation). For addition to a polymer

melt, the layered silicates are usually swollen, making exfoliation much easier than with the dry silicates. The swelling agent has to have a boiling point higher than the melting temperature of the base polymer but noticeably lower than the permissible melt processing temperature. The consistency of the mixture of silicate and swelling agent depends on the silicate/swelling agent relationship, the swellability of the silicate, the type of swelling agent and the temperature, and can range from liquid through slurry to a crumbly paste. By proper employment of nanocomposite in the polymer composition, the following performance advantages can be achieved:

- (A) increased barrier properties to moisture, solvents, chemical vapors, gases such as O₂;
- (B) increased modulus and tensile strength;
- (C) higher heat distortion temperature;
- (D) increased dimensional stability;
- (E) reduced heat release and smoke properties;
- (F) improved flame retardancy;
- (G) improved colorability; and
- (H) improved resistant to whitening or blooming.

EXPERIMENTAL DETAILS

The present composition is further illustrated by preparing laboratory batches and investigating their physical, electrical, and

POLYMER SYSTEM:

Component	Description
PTFE Fluorocarbon	Polytetrafluoroethylene
FEP Fluorocarbon	Fluorinated Ethylene Propylene
PFA Fluorocarbon	Per-Fluoro-Alkoxy Resin
ETFE Fluoropolymer	Ethylene Tetrafluoro Ethylene
PVDF Fluoropolymer	Polyvinylidene Fluoride
ECTFE Fluoropolymer	Ethylene Chlorotrifluoro- ethylene
VLDPE	Very Low Density Polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
HDPE	High Density Polyethylene
PP	Polypropylene
EPR	Ethylene Propylene Rubber
EVA	Ethyl Vinyl Acetate
EEA	Ethylene Ethyl Acrylate
EMA	Ethylene Methyl Acrylate
EBA	Ethylene Butyl Acrylate
MMA	Methylene Methyl Acrylate
PVC	Polyvinylchloride Resin

Filler System: Metal hydrates, oxides, carbonates, talcs, clays, molybdates, borates, stannates, graphites, silicates, phosphates, carbon blacks and nanocomposite organoclays.

Additives: Antioxidants, pigments and lubricants.

The following example compositions were compounded using a laboratory Buss Kneader MKS (30mm). A summary of composition details and test results is set forth in Table I below.

Table I	1	2	3	4	5	6	7	8
Components	phr	phr	phr	phr	phr	phr	phr	phr
PVDF Resin	1-100	1-100	1-100	1-100	1-100	1-100	1-100	1-100
Acrylate Copolymer	1-50	1-50	1-50	1-50	---	---	---	1-50
Acrylate Terpolymer	---	---	---	---	1-50	---	---	---
Ethylene/Acrylic Terpolymer	---	---	---	---	---	1-50	1-50	---
Melamine Octa-Molybdate	---	---	1-50	1-50	---	---	---	1-50
Calcium Molybdate	1-25	1-25	---	---	1-25	1-25	1-25	---
Calcium Carbonate	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5
Polyethylene Wax	0.1-3	0.1-3	0.1-3	0.1-3	0.1-3	0.1-3	0.1-3	0.1-3
Adipate Ester Plasticizer	1-50	---	1-50	---	1-50	---	1-50	---
Antioxidants	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5	0.1-5
Titanium Oxide	0.1-10	0.1-10	0.1-10	0.1-10	0.1-10	0.1-10	0.1-10	0.1-10
Nanocomposite Clay	---	0.1-20	---	0.1-20	---	---	---	0.1-20
Graphite Powder	---	---	---	---	---	---	---	1-20
Brominated Phthalate Plasticizer	---	---	---	---	---	---	1-50	---
Properties								
Specific Gravity	1.69	1.74	1.68	1.73	1.62	1.68	1.62	1.70
Durometer D (Inst./15 sec.)	61/49	66/55	60/48	67/55	51/41	58/48	43/34	66/55
Tensile-Tape	3020	3050	2800	2650	2149	2359	1472	2685
Elongation-Tape	515	525	600	525	465	433	363	210
Air Oven Aging: 7 days @ 165 C								
Ret. Tensile (%)	93	102	NA	NA	NA	NA	NA	NA
Ret. Elongation (%)	89	101	NA	NA	NA	NA	NA	NA
Brittle Point (C)	-22	-14	-25	-18	-33	NA	NA	-2
Oxygen Index (0.125")	50	53	52	57	45.5	52	45.5	62
Smoke (%)	<1	<1	<1	<1	1.2	2.0	1.7	<1
Smoke Color	Lt. Blue	Lt. Blue	Lt. Blue	Lt. Blue	Lt.Grey	Lt.Grey	Lt.Grey	Blue-Grey
Dielectric Constant (1 GHz)	2.88	3.08	2.90	2.92	NA	NA	NA	3.41
Dissipation Factor (1 GHz)	0.057	0.060	0.058	0.054	NA	NA	NA	0.060

The examples in Table I above illustrate batches using PVDF fluoropolymer and olefinic polymers as the base polymer system. The synergistic effect of melamine octa-molybdate and nanocomposite is evident for the above examples 4 and 5. The example 5 demonstrate the benefits of the synergistic effect of having both the melamine octa-molybdate and nanocomposite in the composition. The present technique also permits the production of certain novel flame retardant and low smoke compositions and therefore in a still further aspect the invention, provides a low heat release material. Cone Calorimeter and cable fire tests such as UL-910 tests are used to determine the combustion properties of the various batches. The Cone Calorimeter study is reported in Table II.

**Heat & Visible Smoke Release Rates Using an Oxygen Consumption
Cone Calorimeter**

Table II	Heat Flux (kw/m ²)	Heat Release Rate (kw/m ²)		Smoke Release Rate (m ² /kg)	
		Peak	Average	Peak	Average
Table I (Batch 2)	70	32.9	19	149.1	27.6
Table I (Batch 3)	70	21.2	15.6	77.6	23.2
Table I (Batch 5)	70	23.8	18.1	137.6	17.1

The UL 910 Steiner Tunnel Test has been used for the burning of cables resultant from the selective laboratory batches. These cables were burned according to NFPA 262, Underwriters Laboratories (UL-910), or Canadian Standards Association (CSA FT-6). The example test conditions are as follows: a 300,000 BTU/hour flame is applied for 20 minutes to ten 24-foot lengths of test cables mounted on a horizontal tray within a tunnel.

Detailed example cable test results are summarized in Table III below:

UL 910/NFPA 262 Steiner Tunnel Burn Test Data

Table III

Jacket	Insulation	Smoke		Flame	Cable Construction (Plenum)
		Peak	Average	Spread (ft.)	
Table I (Batch 3)	FR Olefin	0.24	0.06	4.2	4UTP
Table I (Batch 4)	HDPE/Foam	0.32	0.06	5.5	4STP

Table IV below lists batches that are based on a fluoroelastomer, polyvinylchloride and olefinic blend polymer system. These examples also illustrate the synergistic effect obtained by including nanocomposite and melamine octa-

molybdate whereby these blends exhibit enhanced physical, electrical, and combustion properties. The synergistic effect is further evident on example batch 2. This demonstrates the benefits of the synergistic effect of having both the nanocomposite and melamine octa-molybdate in the composition.

Table IV	1	2
Components	phr	phr
PVDF Resin	1-100	1-100
Acrylate Copolymer	1-50	1-50
Ethyl Vinyl Acetate	1-50	1-50
PVC Resin	1-100	100
Melamine Octa-Molybdate	----	1-50
Calcium Molybdate	1-25	----
Calcium Carbonate	0.1-5	----
Calcium Stearate	----	0.1-5
Zinc Stannate	----	1-50
Antimony Oxide LSFR	1-25	1-25
Mineral Filler	1-50	----
Polyethylene Wax	0.1-5	----
Adipate Ester Plasticizer	1-50	1-50
Antioxidants	0.1-10	0.1-10
Titanium Oxide	0.1-10	0.1-10
Nanocomposite Clay	----	0.1-25
Lead Stabilizers	1-15	1-15
Brominated Phthalate Plasticizer	1-75	1-75
Total		
Properties		
Specific Gravity	1.54	1.57
Durometer D (Inst./15 sec.)	64/47	63/47
Tensile-Tape (psi)	2810	3200
Elongation-Tape (%)	385	400
Air Oven Aging: 7 days @ 136 C		
Ret. Tensile (%)	NA	115
Ret. Elongation (%)	NA	90
Brittle Point (C)	-4	-11
Oxygen Index (0.125")	46	52
Smoke (%)	7.8	5.6
Smoke Color	Dark Grey	Dark Grey
Dielectric Constant (1 GHz)	2.64	2.66
Dissipation Factor (1 GHz)	0.024	0.026

The specific embodiment components used in this invention are summarized in Table V.

Table V	Chemical Composition
Components	
PVDF Resin	Vinylidene Fluoride-Chlorotrifluoroethylene Copolymer
Acrylate Copolymer	Methylene Methyl Acrylate Copolymer
Acrylate Terpolymer	Ethylene-Acrylic Ester-Glycidyl Methacrylate Terpolymer
Ethylene Acrylic Terpolymer	Ethylene Methyl Acrylate Terpolymer
EVA Copolymer	Ethyl Vinyl Acetate Copolymer (60% VA)
PVC Resin	Extrusion Grade (IV: 0.90-1.60, RV: 2.10-3.50)
Melamine Octa-Molybdate	Melamine Octamolybdate Powder (particle size: 1-4 micron)
Calcium Molybdate	Calcium Molybdate Powder (particle size: 1-4 micron)
Calcium Carbonate	Calcium Carbonate Powder (particle size: <1 micron)
Calcium Stearate	Calcium Stearate Powder
Zinc Stannate	Zinc Stannate Powder (particle size: 1-4 micron)
Antimony Oxide LSFR	Antimony Oxide Low Smoke (Zinc Modified)
Mineral Filler	Hard and Soft Clays
Polyethylene Wax	Linear Non-Polar Polyethylene Waxes
Adipate Ester Plasticizer	Adipate Ester (Molecular Weight: >2000)
Antioxidants	Hindered Phenolic, Thioester, Phosphate Types
Titanium Oxide	Titanium Oxide Powder (particle size: <1 micron)
Nanocomposite Clay	Cloisite 15A (Southern Clay Products)
Lead Stabilizers	Lead Phthalate and Sulfate powders
Brominated Phthalate Plasticizer	Tribromophthalate, Tetrabromophthalate, tetrabromobenzoate Mixture

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings. It is therefore contemplated by the appended claims to cover such modifications as incorporate those features that come within the scope of the invention.